**Synopsis of the Ph.D thesis entitled**

# "SEMICONDUCTOR WASTE WATER TREATMENT AND RECOVERY OF VALUABLECHEMICALS USING NOVEL TECHNIQUE"

**Submitted to**


Faculty of Engineering & Technology
MGM University, Chhtrapati Sambhajinagar (MS)-431003

By
**HEMANT S. SADAFALE**
(PRN NO. 202101120002)


For the award of Ph.D degree

**DOCTOR OF PHILOSOPHY IN THE SUBJECT OF CHEMICAL ENGINEERING**

Under the guidance of


**Dr. Ravindra W. Gaikwad**
Professor
Department of Chemical Engineering
Jawaharlal Nehru Engineering College
MGM University, Chhatrapati Sambhajinagar (MS)-431003


**April 2024**

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**Introduction:**

The semiconductor industry has been a fast-growing sector of economy in India and many countries around the world due to digitalization. The semiconductor manufacturing involves a large number of complex and highly delicate processes including silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning, etc (1,2,3).The amount of wastewater produced by the semiconductor industry has recently come under strong environmental scrutiny. Microelectronic processes consume millions of gallons of water daily to rinse microscopic dirt and chemicals from the surface of chips. Land disposal of these types of waste are prohibited unless they are pre-treated to Best Available Technology (BAT) standards. Current emphasis is being placed on reducing the amount of waste produced. However, until a more suitable means of production is established, the waste stream must be treated. There are actually several different waste streams that are produced throughout microelectronics manufacturing processes. When considered individually, these wastes are fairly typical and easily treatable. However, due to ongoing research to determine the best way to treat the waste, the individual streams are sometimes combined and stored. This research addresses one potential treatment train applicable to the combined mixed waste stream. More than 200 high-purity organic and inorganic compounds are used in the manufacturing processes of semiconductor industry. Moreover, huge amount of ultrapure water is consumed in various washing and cleaning steps of the semiconductor manufacturing processes. The Table 1 identifies various treatment methods used with some limitations.

**Table No. 1: Identified drawbacks in the treatment of semiconductor wastewater**

| Sr. No | Treatment | Limitations / Drawbacks Identified | Ref. No. |
|---|---|---|---|
| 1 | Biological Process | Inhibit the Micro organisms activity in Biological System | 4 |
| 2 | Eletrodialetic Method | Difficult to applied to Semiconductor Waste Water due to Complexibility of Waste Water | 5 |
| 3 | Precipitation Process | This process can not remove the TAN & Po4 Because it is quickly Intercepted by presence of Po3 So2 & NH 4 | 6 |
| 4. | Coagulation – Flocculation Process | Production of Excess Sludge and uses of large amount of coagulation or conjugate aids | 7 |
| 5. | Adsorption | Require Regular regeneration and hence difficult to recover chemicals from Waste | 8 |
| 6. | Physico-Chemical Treatment of CMP Effluents | Generation of large volumes of metal-bearing sludges or brines that may require future disposal in hazardous waste sites | 9 |
| 7 | Hydroxide precipitation | gelatinous sludge, which is difficult to dewater | 10 |

| | | | |
|---|---|---|---|
| 8 | Sulfide precipitation | It is a more expensive process(chemical costs) and also an excess of sulfide in the effluent could lead to toxicity and corrosion problems | 11,12 |
| 9 | Biosorption | cost of providing nutrients, and toxicity of heavy metals to living cells | 13 |

All the above cited method will not be appropriate to take care of the waste water; in addition these turn into expensive methods for its industrial scale-up operation. The conventional treatment methods adopted for removal of metals depend upon the maintenance of the toxic limit of metal concentration and adequate acclimatization of the bio-mass. The trickling filter and the activated sludge process are generally in use for the treatment of industrial waste water. In activated sludge process the requirement of air for aeration increase with waste concentration. The heavy metal loading removal is effective only up to a certain level. The discharged effluent standard being 0.1 mg/lit, the conventional methods are not efficient to bring down the heavy metals concentration to such a low level in the treated effluent. To overcome this problem, there is an urgent need of design of the wastewater treatment plant. This research aims at development of appropriate technological protocol for treat the semiconductor industry wastewater.

**Objective:**

- Characterization of wastewater.
- Design and fabrication of Equipment/column for the Treatment of wastewater stream from semiconductor manufacture.
- Effect of different concentrations on removal.
- Effect of pH of solution.
- Effect contact time.
- Effect of types of resins or zeolite.
- Effect of flow rates.
- Modelling & Simulation of the Process.
- Recovery of chemicals and heavy metals.

**Scope of Work:**

The scope of this study is to intend to treat the wastewater stream from semiconductor manufacture facility with special reference to heavy metal removal & its recovery. The performance of a fixed-bed column can be defined and the characteristic breakthrough curve of the ion exchange phenomena is to be achieved through mathematical model. The flow of work is given in Fig. 1.

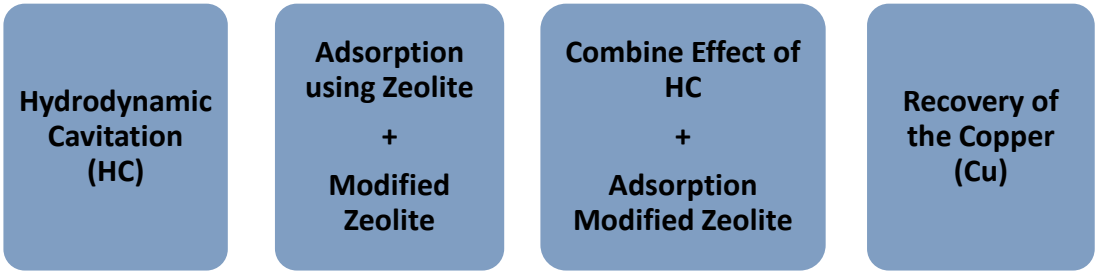


**Fig 1: Scope of work**

**Work done:**

- Procurement of Wastewater samples from the C-MET
- Characterization of Wastewater Sample water
- Design & Fabrication of Equipment for both hydrodynamic cavitation & adsorption
- Experimentation on Hydrodynamic Cavitation
- Experimentation by adsorption using natural Zeolite
- Experimentation by using natural modified Zeolite
- Experimentation on combined effect of hydrodynamic cavitation & adsorption modified Zeolite
- Recovery of heavy metal Cu.
- Modelling & Simulation of the Process
- Organization of data, results, and discussion.

**Contribution made to the existing knowledge on the subject:**

- **Novel Findings:** The thesis may present new empirical data, experimental results, or observations that were previously unknown or not well-documented for semiconductor industry wastewater.
- **Addressing Gaps in Knowledge:** This work may fill gaps in existing literature or provide new insights into areas that were understudied or underexplored for semiconductor industry wastewater treatment.
- **Practical Applications:** The research might have implications for real-world applications or offer solutions to practical problems of semiconductor industry wastewater.
- **Critical Analysis:** The thesis might critically evaluate existing theories, methodologies, or practices, leading to a deeper understanding of the subject matter.
- **Integration of Knowledge:** It might synthesize diverse sources of information and integrate knowledge from different disciplines to provide a comprehensive understanding of a complex issue.
- **Policy Implications:** The findings might have policy implications, informing decision-makers and influencing policy development water & wastewater treatment industries.
- **Generalizability:** The research might demonstrate the generalizability of findings beyond the specific case studied, contributing to broader knowledge.
- **Development of IPR:** This research contributed towards the 1 Patent publications, 1 Paper presented, 1 paper published in SCOPUS journal and 1 Paper accepted for publication in SCOPUS journal.

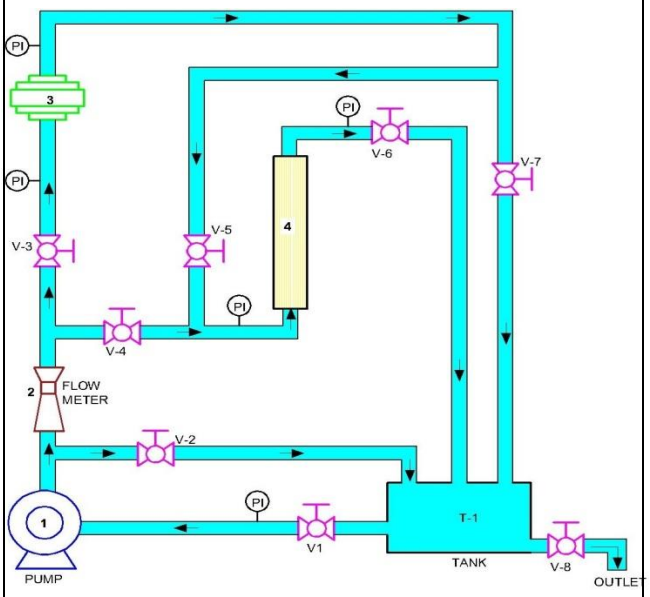


**Fig.2: Experimental Set up**

| Nos. | Particulars |
|---|---|
| 1 | Pump (1 Hp) Horizontal Suction Vertical Discharge |
| 2 | Flow Meter |
| 3 | Cavitation device |
| 4 | Adsorption Bed |
| T1 | Tank |
| V-1 To V-8 | Valve (Controlling Device) |
| PI | Pressure Indicator |

**Table 2: Details about experimental set up**

**Experimental Setup**

The experiment setup consists of Pump, flow measurement, cavitation device (orifice plate), adsorption bed, tank, pressure indicator, and valves (controlling device).The cavitation, adsorption study conducted individually and the combined study was carried out in same apparatus. During the cavitation study the adsorption column was kept closed. The schematic diagram of experimental set up has been shown in the Fig.2. The hydrodynamic cavitation reactor used in the work consists of a reservoir or a collecting tank with 50 L capacity and the flow of feed is controlled by Valve V-1. First the feed is taken in tank and the settled sludge is taken out by Valve V-7 then the remaining is passed to equalization tank by T-1. The $H_2O_2$ was added as an oxidizing agent to in equalization tank T-1 to increase the rate of reaction. The feed is connected to the pump (rating of 1 HP) through Valve V-3 and the pressure was controlled by pressure gauge PI which allows re-circulation of the contents through a mainline housing an orifice plate and a recycle line using valve V-2 (for controlling the inlet pressure and the flow rate into the cavitation chamber) by keeping Valve V-4 closed. The pressure difference ($\Delta P$) across the orifice plate was maintained by pressure gauge Inlet PI and Outlet PI of the cavitation Device; the sample was collected through V-7in regular interval of time which is recycled to equalization tank. Due to pressure difference the bubbles form i.e. pressure excides atmospheric pressure and there is transient collapse of bubbles. For a instant pressure at orifice plate increases up to 5 bar and temperature 6 to 7 thousand Kelvin which generates $OH^-$ radicals which are highly reactive and due to oxidation process with high rate of reaction decomposes the Cu.. The

highly reactive $OH^-$ radical reacts with feed which decreases the BOD and COD of feed. During the separate adsorption column study valve V-1,V-4,V-6 are kept open and feed was passed through adsorption column. The treated feed was collected by valve V-6 and recycled through V-1 from equalization tank. The collected sample was analyzed and the BOD, COD was determined. In combined study of cavitation and adsorption the feed was firstly passed through orifice plate and then by opening valve GB-08 the treated outlet was given as a feed to adsorption column by keeping valve V-4, V-7 closed. The treated feed was taken out through valve V-5 and Valve V-1 was used for recycling. The side view and Front view of equipment is shown in Fig. 3 and Fig.4 respectively. Fig. 5 and Fig.6 shows orifice seat and plates used in experimentation.

**Fig.3. Side view of Experimenatl Model**

**Fig.4. Front view of Experimenatl Model**

**Fig. 5. Orifice Seat**

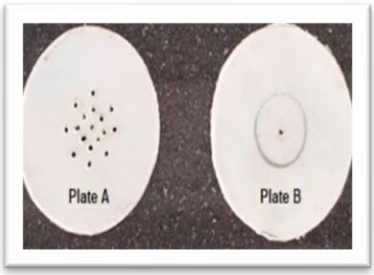


**Fig. 6. Orifice Plate-A and Plate-B**

**Hydrodynamic Cavitation study**

One of the alternative techniques for the generation of cavitation is the use of hydraulic devices where cavitation is generated by the passage of the liquid through a constriction such as orifice plate. Studies show that HC, when combined with other chemical oxidants like $H_2O_2$, Ozone, Persulfates, Fenton's Reagent, and peracids etc. significantly enhances mineralization efficiency. The oxidant itself is oxidised to produce reactive $OH^{\cdot}$ radicals.

$$H_2O_2 + Cavitation \rightarrow HO + HO^{\cdot}$$

This study uses orifice plate of 1mm hole of waste water samples using inlet pressures of 1 to 6 bar. Since the pollutants water is complex, all results are expressed as a percentage reduction in COD and BOD of samples collected at regular intervals. With an increase in pressure from 3 to 5 bar, the percentage reduction in BOD and COD increased from 27 to 39 and 29.7 to 48.9 % respectively shown in Table No. 3.

**Table No.3: Details of Flow Characteristics of Plate A**

| Inlet Pressure (Bar) | Volume Flow Rate (LPH) | Velocity (m/s) | Cavitation Number (CV) | % COD Removal |
|---|---|---|---|---|
| 1 | 170 | 16.08 | 0.59 | 15.7 |
| 2 | 210 | 20.92 | 0.47 | 21.7 |
| 3 | 260 | 24.35 | 0.37 | 29.7 |
| 4 | 310 | 27.1 | 0.26 | 38 |
| 5 | 360 | 31.35 | 0.19 | 48.9 |
| 6 | 410 | 44.65 | 0.08 | 46 |
| 7 | 460 | 59.67 | 0.03 | 39 |

**The Influence of Inlet Pressure on BOD and COD breakdown:**

When inlet pressure rises, the flow rate in the main line also rises, as shown in Fig. 7. For each plate's configuration, a different rise in flow rate occurs. According to Fig. 7, reduction of BOD and COD for both plates increases with an increase in inlet pressure from 2 bars to 5 bars over a fixed period of 2 h. After then, as the inlet pressure rises higher, the degrading efficiency begins to decrease or decline. This is brought on by a process known as super cavitation, in which vapour clouds are formed in the line when bubbles produced in hydrodynamic cavitation reactors do not detonate.

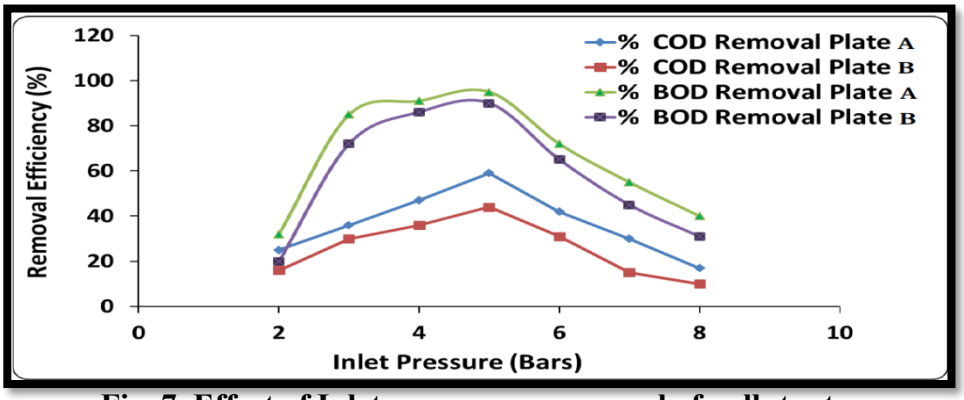


**Fig. 7. Effect of Inlet pressure on removal of pollutant**

**The Influence of Reaction Time:**

Fig. 8 describes the impact of reaction time on the degradation of BOD and COD. When the efficiency of the two orifice plates is compared, it can be seen that plate 1 has a higher efficiency because there is more cavitational interaction and a more violent collapse of cavities, which results in better Hydroxyl Radicals. This extra hydroxyl aids in the elimination of pollutants such as COD and BOD. At the end of an hour, it was found that orifice plate 1 produced greater COD and BOD elimination of 58% and 88%, respectively.,

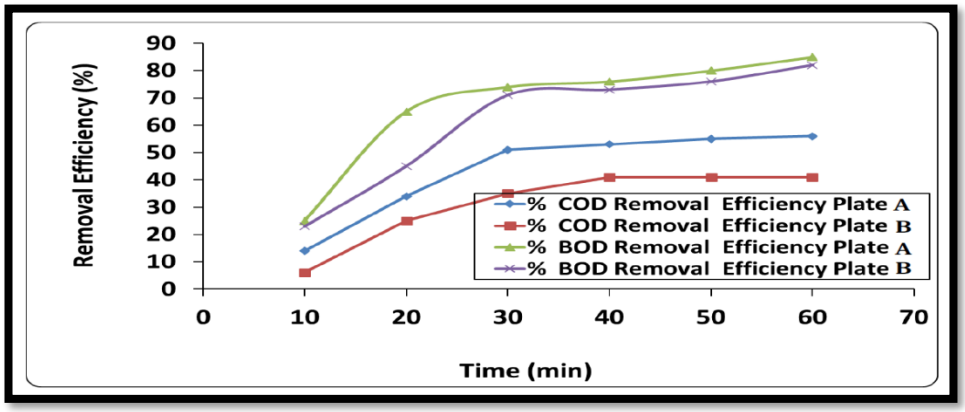


**Fig. 8. Effect of reaction time on removal efficiency**

**Adsorption using natural Zeolite**

One of the most promising and recently suggested methods is adsorption using natural or modified zeolites [14]. Zeolites have a high porosity and naturally occur at a low cost. In general, there are more than 60 types of natural zeolites [15]. Natural zeolites can be used to reduce turbidity and color and degrade ammonium, heavy metal cations, and other cationic pollutants [16].

**Modification of Zeolite**: A modification of zeolite done using Acetone and cellulose acetate in proportion of 2:1 for duration 24 hours. The percentage adsorption of copper ions decreases with increase in pH while for zeolite and for modified zeolite, the percentage of adsorption increase with increase in pH. In case of modified zeolite the maximum removal is observed at high pH it is due to increase of active sites on the zeolites, hence the rateof copper ions sorption is maximum on the active surface due to cation exchange phenomenon of modified zeolite at high pH value. The removal was found to be 80,75,70,60 and 50 for zeolites at pH 2,4,6,8,10 respectively and for modified zeolite the removal was found 75,80,85,90 and 95 at pH 2, 4,6,8,10 respectively.

**Characterization of Adsorbents:** Before and after the experimentation, the characterization of zeolites (virgin and modified) have been done such as XRD, FTIR , BET and SEM.

**Batch Adsorbent Study:**

**Effect of pH** It was observed in the present investigations that with the increase in pH of the solution, the extent of copper ions removal increased in the cases of modified zeolite adsorbent.(Fig. 9). The removal was found to be 80,75,70,60 and 50 for zeolites at pH 2,4,6,8,10 respectively and for modified zeolite the removal was found 75,80,85,90 and 95 at pH 2, 4,6,8,10 respectively.

**Effect of Adsorbent dosage:** The effect of adsorbent dosage on the adsorption of Cu (II) ions is depicted in Figure 10. For Cu (II) ions, the removal percentage rises as adsorbent dosages rise. This

might be the result of the higher concentration of adsorbents in the solution having a larger surface area and more exchangeable sites available for the ions. At a dosage of 12 g/L for Cu (II) ion, zeolite and modified zeolite were able to remove the highest proportion of Cu (II) ions by 85%.

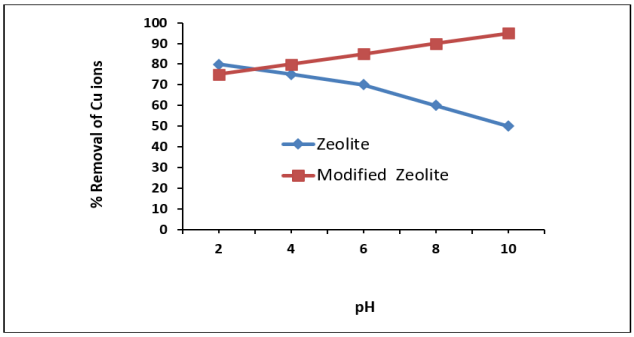


Fig 9: Effect of pH on the Removal of copper ion using Zeolites

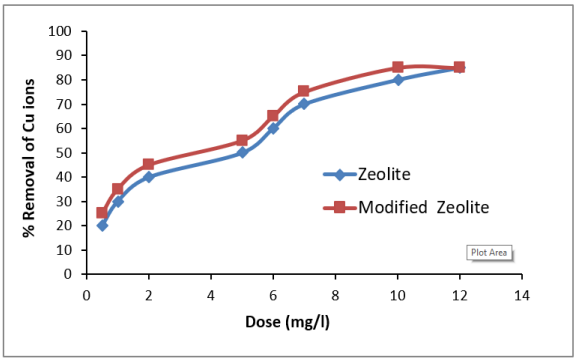


Fig. 10: Effect of Adsorbent dose on the Removal of Copper ion using Zeolites

**Column Adsorption Study:**

**Fig. 11.Packed bed with 6, 9 and 12 inch diameter**

Different bed lengths were used during the experimentation such as 6 inch, 9 inch ,12 inch as shown in Fig. 11. A natural Zeolite Calcium aluminosilicate (CAS)($Ca4.5Na_3[ (AIO_2)12(SIO_2)12]XH_2O$) is naturally occurring silicate clay used during this experiment. wastewater sample allow to pass from each bed height with virgin zeolite Calcium aluminosilicate. Treated water sample was collected after every 10 min. .

**Combined Study of Hydrodynamic Cavitation and Adsorption using modified zeolite**

Combined study of hydrodynamic cavitation and adsorption using modified zeolite having bed height 12 inch is done. Increase in TDS will be nullified and can be treated by the modified zeolite which leads to decrease in TDS. In this study a continuous combined (cavitation and adsorption in combination) have been carried out. By varying the different parameters such as effect of pH, contact time &initial concentration of heavy metal on the % removal of Cu, was studied. The experiments were carried out for various pH from 1 to 7, concentration 30 to 70mg/lit and time of 180min. The faster degradation of Cu, in the hydrodynamic cavitation, the experiments were carried out with addition of 70 ml/l $H_2O_2$ to generate large amount of free radical. The decrease in BOD and COD

was also studied in this process. The study aims to achieve targeted results in the removal of pollutants from semiconductor water by combining a Cavitation with an Adsorption column in continuous study. For the combine study both the hydrodynamic cavitation and adsorption have been used in a continuous mode. First the semiconductor waste water was passed through the orifice plate and then passed through the adsorption column for degradation of heavy metals wastewater. Studies have been conducted for, the effect of concentration, effect of pH and effect contact time.

**Recovery of Cu**

This process is in essence a four-step operation. In the first step, Cu is adsorbed onto the solid resin phase by exchange with H which is combined with H+ in the aqueous solution to form $H_2SO_4$. In the second step, the exhausted resins are regenerated using 5 wt % HCL and the adsorbed Cu in the

solid phase is replaced by H and is detached and combines with Cl- in the aqueous solution to form $CuCl_2$ . The recovery of chemical process depicted in Fig. 12.

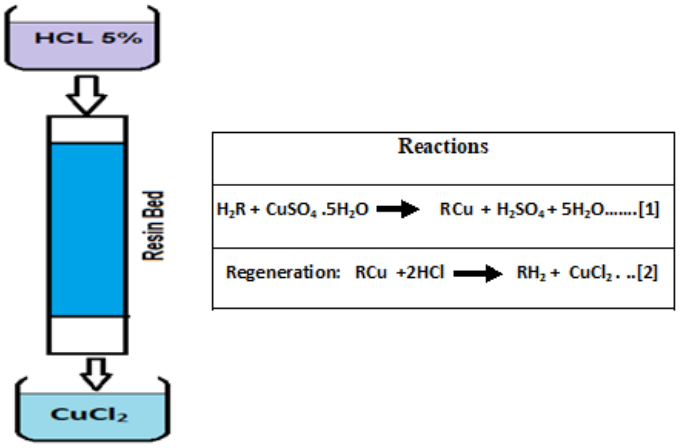


**Fig.12. Recovery of Chemical**

RH represents the H-type ion exchange resin. It is noted that between the adsorption and desorption steps,**$CuSO_4$** in the original waste acid solution is significantly converted to form $CuCl_2$ after desorption, as shown in the second reaction

**Modelling & Simulation:**

A generalized model that incorporates external film mass transfer resistance and pore diffusion resistance with the variation of bed height has been formulated and solved of semiconductor wastewater containing heavy metal, Cu(II).

**Principal Conclusion:**

A novel hybrid system based on HC and adsorption was successfully applied for the treatment of semiconductor industry wastewater. In this work the removal of heavy metal, Cu was carried out

using hydrodynamic cavitation and adsorption. Effects of different process variables such as initial concentration, solution pH, time and addition of $H_2O_2$ on the removal of heavy metals were studied. The removal of heavy metal, Cu was found to be pH dependent and basic medium was found to be favourable for the higher removal of heavy metals. It was found that operating pH, state of molecule (whether molecular or ionic) and nature (hydrophobic and hydrophilic) are the important parameters which ultimately decide the efficient degradation of pollutants. Following are the overall conclusion.

- Under optimized conditions, combined treatment schemes typically yield superior results compared to individual oxidation processes.
- Combined wastewater treatment system based on HC and packed bed zeolite adsorption were studied for the removal of BOD and COD. BOD and COD removal was achieved up **to 92 % and 72 %** respectively.
- The operating parameters of HC, such as inlet pressure, pH of the solution etc. play a crucial role in deciding the effectiveness of treatment and final obtained extent of degradation.
- A recovery of the valuable heavy metals is investigated and found 32%.
- Modeling & Simulation of the process have been done.
- Finally this work demonstrates the effectiveness of hydrodynamic cavitation in removing pollutants from semiconductor wastewater streams, either in combination with adsorption/ion exchange processes.

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HSSadafale

**Research Scholar**
**Mr. Hemant S. Sadafale**
(PRN NO. 202101120002)

**Guide**
**Dr. Ravindra W.Gaikwad**
Professor
Department of Chemical Engineering
Jawaharlal Nehru Engineering College
MGM University, Chhatrapati Sambhajinagar (MS)